

## Strategies for Standardizing EDS Measurements

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Energy dispersive X-ray spectrometers (EDS) are capable of precise and accurate electron beam measurements of composition. However, the optimal strategies for acquiring EDS standards differ from its wavelength dispersive cousin. There is a lot more information in an EDS spectrum that can be used to evaluate its quality. This information can be used to perform inter-comparisons between multiple spectra collected from the same material.

When collecting an EDS standard, the goal is to create a single spectrum that best represents the material in both intensity and shape. The most direct path is not necessarily the best. Rather than measure a single spectrum for a long duration  $\tau$ , it is often better to spend the same instrument time and collect  $M$  spectra each for a duration  $\tau/M$ . The  $M$  spectra can be compared to one another, and a sum spectrum constructed from the subset of the  $M$  spectra that are deemed sufficiently similar. Similarity does not guarantee optimality. However, similar spectra are more likely to be optimal as there is only one way to measure the optimal spectrum and many ways to measure a bad spectrum. This strategy requires a mechanism for comparing spectra for similarity that is independent of dose and relative scale.

EDS measurements are believed to obey the basic assumptions for a Poisson process both in aggregate and on a channel-by-channel basis. For large numbers of events, the Poisson distribution approaches the Normal distribution with the same variance. Using this information, we can create a metric to compare spectra channel-by-channel. The difference of two spectra collected for identical times at the same probe current at two points on a homogeneous, flat polished material is bound on the lower end by the limit imposed by the Poissonian process. The strategy is therefore to compare each spectrum in a set of  $M$  nominally identical spectra with the sum of the other  $M - 1$  spectra and give each spectrum a score which has a lower bound of approximately 1 when the spectra differ only by Poisson statistics. Such a metric is the mean reduced  $\chi^2$  statistic [1] defined by

$$\chi_{\nu}^2 = \frac{1}{N} \sum_{i=1}^N \frac{(S_{1,i}/d_1 - S_{2,i}/d_2)^2}{S_{1,i}/d_1^2 + S_{2,i}/d_2^2}$$

where  $N$  is the number of channels,  $S_{j,i}$  is the number of X-ray events in the  $i$ -th channel of the  $j$ -th spectrum and  $d_j$  is the probe dose (probe current  $\times$  live time.) The sum may be over all channels in the spectrum or, better yet, those channels representing the informative part of the spectrum (see Table 1).

Spectra with  $\chi_{\nu}^2$  scores closer to unity are more similar and more likely to truly represent the ideal spectrum. Removing spectra with high scores and recomputing the metric for each remaining spectrum allows you to iteratively evaluate a set of spectra until a self-consistent set is found.

This strategy has been implemented in DTSA-II's Spectrum Bundler[2] and in NeXLSpectrum's `similarity(...)` and `findsimilar(...)` functions [3] (<https://github.com/usnistgov/NeXLSpectrum.jl>). In

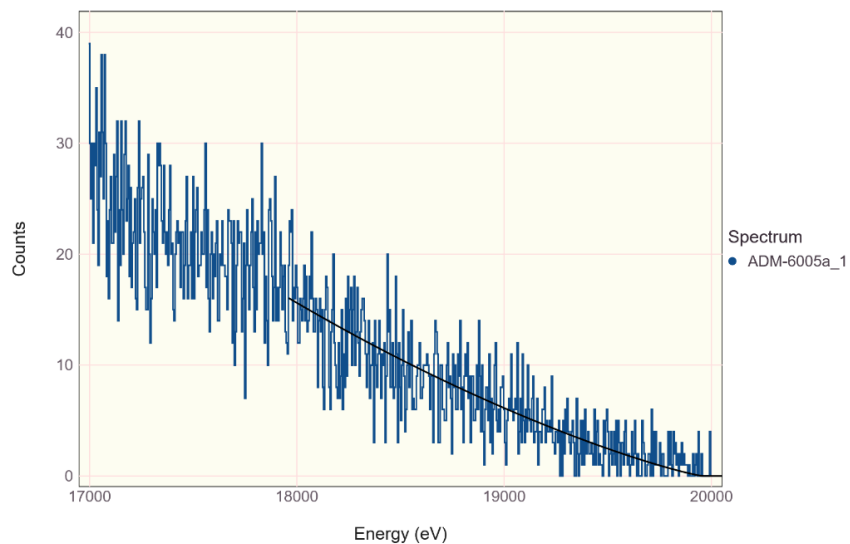
practice, careful measurements on ideal samples will produce  $\chi^2_\nu$  metrics that are close to unity. Rougher surfaces, inhomogeneous samples or surface contamination are the most common reasons that spectra have metrics significantly larger than unity. With materials that are truly inhomogeneous, like some natural mineral standards, it can be necessary to accept  $\chi^2_\nu$  metrics far from unity.

In addition, the Duane-Hunt limit [4] should be checked on every measured spectrum. The Duane-Hunt limit is the energy at which the signal from the X-ray continuum goes to zero (see Figure 1.) Conservation of energy limits the maximum energy of continuum X-rays to less than the incident electron energy. X-rays approaching the incident electron beam energy are increasingly rare, so the signal is necessarily small. Regardless, it is possible to fit a continuum model to the last couple thousand electronvolts of the continuum signal and in this manner estimate the Duane-Hunt. The estimated Duane-Hunt can be compared to the nominal beam energy. Significant disparities should be investigated as they may reflect an incident beam energy less than intended (as, for example, sample charging). The characteristic intensity depends strongly upon the incident beam energy (particularly at low overvoltage).

Spectra that pass both the  $\chi^2_\nu$  test and the Duane-Hunt test are likely, when summed, to produce representative standards in which you can have a high degree of confidence. EDS spectra can also be used in a similar manner as a quality control mechanism when standardizing WDS. Wavelength measurements associated with disparate spectra should be considered for culling.

Spectrum	C	O	Mg	Al	Si	Ca	Fe	All	Mean
III K412[0][all]	0.7529	1.5103	1.1503	1.2335	1.1775	1.4786	0.9892	1.0427	1.1846
III K412[1][all]	0.9918	1.2388	1.0210	1.1505	1.8115	1.0310	0.9823	1.0069	1.1753
III K412[2][all]	0.6158	0.6653	1.1114	1.0077	1.2456	1.1176	1.0226	1.0034	0.9694
III K412[3][all]	1.0227	1.3338	0.5570	0.9520	1.6270	1.1942	0.9105	0.9953	1.0853
III K412[4][all]	0.7759	2.0676	0.9516	0.8981	0.9972	0.8413	1.1358	1.0025	1.0953

**Table 1.** Comparing 5 spectra collected from K412 glass using the  $\chi^2_\nu$  metric over ranges of channels corresponding to the elements in the column headers. The All and Mean columns reflect the  $\chi^2_\nu$  metric over 100 eV to  $E_0$  and the mean of all element metrics, respectively. These spectra compare nicely over all elements. The largest metric is for the O in the last row and even this is only approximately twice what we'd expect from count statistics alone.



**Figure 1.** The high energy tail of a spectrum collected from ADM-6005a glass showing the best fit continuum model from which the Duane-Hunt can be extracted. (In this case, 19.96 keV - very close to 20keV.)

References:

- [1] Taylor, J.R., Error Analysis, Univ. Science Books, (Sausalito, CA).
- [2] Ritchie, N.W.M., Mengason, M.J. and Newbury, D.E., *Microscopy and Microanalysis* **23** (2017), p. 220.
- [3] Ritchie, N. W. M., Reproducible Spectrum and Hyperspectrum Data Analysis using NeXL, accepted for publication, *Microscopy and Microanalysis* (2022).
- [4] Duane, W. & Hunt, F.L., *Physical Review* **6** (1915).